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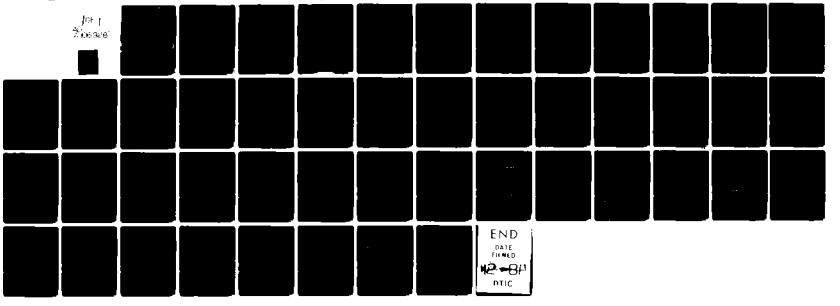

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Electrodes can be functionalized with {N,N'-Bis(-3-(trimethoxysilyl)propyl)-4,4'-bipyridinium}dibromide, I, yielding a surface-confined, electroactive polymer, $(PQ^{2+}\cdot 2Br^-)_n$. The anions are labile and can be replaced readily by a number of anions. By a combination of Auger and electrochemical techniques we have studied the incorporation of the anions: p-toluenesulfonate, $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$, $SCN^-$, $SO_4^{2-}$, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Co(CN)_6^{3-}$, $Mo(CN)_8^{4-}$, $IrCl_6^{2-}$, and $PtCl_6^{2-}$ into $(PQ^{2+})_n$. Generally, the transition metal complex anions are more firmly bound and less labile than the other anions. The ordering of monoanions is p-toluenesulfonate $\approx Cl^- < Br^- \approx ClO_4^- \approx SCN^- < I^-$. The $SO_4^{2-}$ anion competes well with $ClO_4^-$ and not as well with $I^-$. For the monoanions and $SO_4^{2-}$ the selectivity for binding spans a range of apprxoimately an order of magnitude. For example, a solution having 0.09 M $Cl^-$ and 0.01 M $I^-$ has ~50% $I^-$ and ~50% $Cl^-$ in the $(PQ^{2+})_n$. The selectivity for binding $IrCl_6^{2-}$, the most weakly bound transition metal complex, is considerable. For example, a solution having 0.1 M $SO_4^{2-}$ and $5 \times 10^{-5}$ M $IrCl_6^{2-}$ gives >50% $IrCl_6^{2-}$ in the $(PQ^{2+})_n$ when analyzed by Auger spectroscopy after removal from the solution followed by washing. The complexes $Mo(CN)_8^{4-}$, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $IrCl_6^{2-}$ exhibit chemically reversible redox reaction when bound to the polymer, as determined by cyclic voltammetry. Such electroactive anions can be bound in the $(PQ^{2+})_n$ polymer for prolonged periods (>1 h) in the presence of 0.1 M KCl. Cyclic voltammetry of electrodes having variable amounts of $IrCl_6^{3-}$, $(PQ^{2+}\cdot \frac{2}{3} \times IrCl_6^{3-} + (1 - x)SO_4^{2-})_n$ (x = 0-1), correlates well with intensity of Auger signals characteristic of $IrCl_6^{3-}$ relative to those for $(PQ^{2+})_n$, providing confidence in our use of Auger to order the binding of nonelectroactive anions. Electrochemistry allows an ordering of $IrCl_6^{2-} < Fe(CN)_6^{4-} \approx Ru(CN)_6^{4-} < Mo(CN)_8^{4-}$ for the electroactive ions. The effect of $Co(CN)_6^{3-}$ on the electrochemistry of $Fe(CN)_6^{4}$ and $Mo(CN)_8^{4-}$ places $Co(CN)_6^{3-}$ near $Ru(CN)_6^{4-}$ in this ordering.

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by

James A. Bruce and Mark S. Wrighton

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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# Electrostatic Binding of Electroactive and Nonelectroactive Anions in a Surface-Confined, Electroactive Polymer: Selectivity of Binding Measured by Auger Spectroscopy and Cyclic Voltammetry

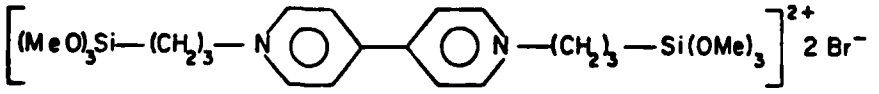
James A. Bruce and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 U.S.A.

Abstract: Electrodes can be functionalized with {N,N'-Bis(-3-(trimethoxysilyl)propyl)-4,4'-bipyridinium}dibromide, I, yielding a surface-confined, electroactive polymer, $(PQ^{2+}\cdot 2Br^-)_n$. The anions are labile and can be replaced readily by a number of anions. By a combination of Auger and electrochemical techniques we have studied the incorporation of the anions: p-toluenesulfonate, $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$, $SCN^-$, $SO_4^{2-}$, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Co(CN)_6^{3-}$, $Mo(CN)_8^{4-}$, $IrCl_6^{2-}$, and $PtCl_6^{2-}$ into $(PQ^{2+})_n$. Generally, the transition metal complex anions are more firmly bound and less labile than the other anions. The ordering of monoanions is p-toluenesulfonate $\simeq Cl^- < Br^- \simeq ClO_4^- \simeq SCN^- < I^-$. The $SO_4^{2-}$ anion competes well with $ClO_4^-$ and not as well with $I^-$. For the monoanions and $SO_4^{2-}$ the selectivity for binding spans a range of approximately an order of magnitude. For example, a solution having 0.09 M $Cl^-$ and 0.01 M $I^-$ has ~50% $I^-$ and ~50% $Cl^-$ in the $(PQ^{2+})_n$. The selectivity for binding $IrCl_6^{2-}$, the most weakly bound transition metal complex, is considerable. For example, a solution having 0.1 M $SO_4^{2-}$ and $5 \times 10^{-5}$ M $IrCl_6^{2-}$ gives >50% $IrCl_6^{2-}$ in the $(PQ^{2+})_n$ when analyzed by Auger spectroscopy after removal from the solution followed by washing. The complexes $Mo(CN)_8^{4-}$, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $IrCl_6^{2-}$ exhibit chemically reversible redox reaction when bound to the polymer, as determined by cyclic voltammetry. Such electroactive anions can be bound in the $(PQ^{2+})_n$ polymer for prolonged periods (>1 h) in the presence of 0.1 M KCl. Cyclic voltammetry of electrodes having variable amounts of $IrCl_6^{3-}$, $(PQ^{2+}_{\frac{2}{3}}xIrCl_6^{3-} + (1-x)SO_4^{2-})_n$ (x = 0-1), correlates well with intensity of Auger signals characteristic of $IrCl_6^{3-}$ relative to those for $(PQ^{2+})_n$, providing confidence in our use of Auger to order the binding of nonelectroactive anions. Electrochemistry allows an ordering of $IrCl_6^{2-} < Fe(CN)_6^{4-} \simeq Ru(CN)_6^{4-} < Mo(CN)_8^{4-}$ for the electroactive ions. The effect of $Co(CN)_6^{3-}$ on the electrochemistry of $Fe(CN)_6^{4}$ and $Mo(CN)_8^{4-}$ places $Co(CN)_6^{3-}$ near $Ru(CN)_6^{4-}$ in this ordering.

Electrodes derivatized with electroactive polymers or with charged, nonelectroactive polymers can be significantly influenced by the nature of the electrolyte and other ions present in a solution contacted by the derivatized electrode. It has been shown that charged, nonelectroactive polymers can persistently bind significant quantities of charged, electroactive species such as $Fe(CN)_6^{4-}$ by surface polyvinylpyridinium[1-3] or $Ru(bipyridine)_3^{2+}$ by Nafion.[4] These examples illustrate how electrostatic binding may be exploited for analysis, preparation of a variety of modified electrodes, and study of electrocatalysis. Electroactive polymers are charged in at least one of their accessible redox states and both selectivity of counterion binding and the movement of ions in and out of the surface polymer associated with change of redox state may affect electrochemical behavior.[5-7] Electrodes coated with electroactive polymers may have a number of uses,[8] including desalting of $H_2O$,[9] that depend on the behavior of solution ions.

Recent work in this laboratory[10,11] has involved the use of reagent I



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to functionalize photocathode surfaces yielding a surface-confined electroactive polymer, $(PQ^{2+}.2Br^-)_n$. The ability to observe essentially reversible redox chemistry for the $(PQ^{2+})_n$ in aqueous KBr suggests good mobility for the anions, equation (1a) and/or the cations, equation (1b).

$$\text{surface-}(PQ^{2+}.2Br^-)_n + ne^- \xrightleftharpoons{\text{-0.5 V vs. SCE}} \text{surface-}(PQ^{+}.Br^-)_n + nBr^- \quad (1a)$$

$$\text{surface-}(PQ^{2+}.2Br^-)_n + ne^- + nK^+ \xrightleftharpoons{\text{-0.5 V vs. SCE}} \text{surface-}(PQ^{+}.K^+.2Br^-)_n \quad (1b)$$

We exploited the lability of the anions to incorporate Pt(0) in the polymer as a hydrogen evolution catalyst,[11] equations (2) and (3). In this

$$\text{surface-}(PQ^{2+}.2Br^{-})_n + nK_2PtCl_6 \rightarrow \text{surface-}(PQ^{2+}.PtCl_6^{2-})_n + 2nKBr \quad (2)$$

$$\text{surface-}(PQ^{2+}.PtCl_6^{2-})_n \xrightarrow[KBr]{\text{reduce}} \text{surface-}(PQ^{2+}.2Br^{-}/Pt(0))_n + 6nCl^{-} \quad (3)$$

article we put our preliminary results for $PtCl_6^{2-}$ incorporation on a quantitative footing and amplify our studies of ion exchange involving both electroactive and nonelectroactive anions. Of particular importance is the establishment of Auger spectroscopy as a good tool for determining the presence, and relative amount, of ions such as $Cl^-$, $Br^-$, etc. that are difficult to determine by other techniques. It has been claimed that X-ray photoelectron spectroscopy is a useful technique to detect such anions on modified electrode surfaces.[12] The electrodes that have been studied are Pt and p-type Si,[11] but the results should be directly extendable to any other surface modified with I.

## Experimental

Electrodes and Derivatization. Single crystal p-Si wafers (0.35 mm thick, (111) face exposed) doped with B (resistivity, 3-7 ohm-cm), were obtained from Monsanto Co., Electronics Division (Palo Alto, CA). Ohmic contact to the back of the electrode was made by vapor deposition of Al then sintering at 723 K under $N_2$ for 5 min. Electrodes were mounted as previously described.[10,11] Typical electrode areas ranged from 10-25 $mm^2$.

Synthesis of I has been previously described.[10,11] For derivatization of Si, the Si electrodes are first etched in concentrated HF at 298 K for 60 s then rinsed in distilled $H_2O$ and dipped in 10 M NaOH at 298 K for 60 s. The electrode is then rinsed again in distilled $H_2O$, followed by acetone and air dried. The electrodes are then immersed into a 1-5 mM solution of I in $CH_3CN$ under $N_2$ and left for 3-48 hrs at 298 K. After removal from solution, the electrodes are rinsed with $CH_3CN$ and stored under Ar. Pt foil electrodes are electrochemically pretreated as previously described.[13] Pt electrodes were then derivatized with I either by immersion into 1-5 mM solutions of I in $CH_3CN$, or by potentiostatting the electrodes at -0.72 V vs. SCE in aqueous 0.1 M $K_2HPO_4$, 0.2 M KCl, ~3 mM I. Coverage of electroactive $(PQ^{2+})_n$ was determined by integration of the cyclic voltammetric wave associated with $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$

Electrochemical Equipment. Cyclic voltammograms were obtained using a PAR model 173 potentiostat, a model 175 programmer, and a Houston Instruments 2000 XY recorder. All experiments were performed in a single compartment Pyrex cell equipped with a saturated calomel reference electrode (SCE), a Pt wire counter-electrode, and a Pt or p-Si working electrode. The solution contained 0.1 M supporting electrolyte. Reagent grade chemicals and distilled, deionized $H_2O$ were used. Studies involving electrodes derivatized with I were carried out under Ar. P-Si electrodes were illuminated with a beam expanded 632.8 nm He-Ne laser (Aerotech or Coherent Radiation) providing up to ~50 $mW/cm^2$.

Ion Exchange Into $(PQ^{2+})_n$ Polymer. Replacing the $Br^-$ in $(PQ^{2+}.2Br^-)_n$ by another anion was accomplished by placing the electrode into an aqueous solution of the appropriate ions. The electrode was then left to equilibrate at 298 K for a period of time long enough to insure that equilibrium was established. The electrode was then well-rinsed with distilled, deionized $H_2O$ to remove any excess electrolyte.

Auger Spectroscopy. Auger spectra were obtained on a Physical Electronics Model 590A scanning Auger spectrometer. A 5 keV electron beam with a beam current of from 0.3 to 1 μA was used as the excitation source. Si samples were mounted by attaching the Cu wire lead to the sample holder, and Pt samples were clipped down to insure electrical grounding. The pressure was maintained at $<10^{-8}$ torr during analysis. A 3 keV electron beam was used in a few samples where charging was a problem.

Depth profiling using an Auger spectrometer has been previously described.[14] A Physical Electronics Model 04-303 differential ion gun was used to produce a 2 keV $Ar^+$ ion beam for sputtering. The pressure was maintained at ~$3 \times 10^{-7}$ torr in the main vacuum chamber, and $1.5 \times 10^{-4}$ torr of Ar in the ionization chamber. Generally, signals for C, N, O, Si, the counterion of $(PQ^{2+})_n$, and the substrate (Si or Pt) were analyzed as a function of sputtering time.[15] The energy window used was typically 10-50 eV around the energy characteristic of the element being analyzed. The Auger signals (and their energies) monitored during depth profiles are as follows: C (273 eV); N (379 eV); O (503 eV); Cl (181 eV); S (152 eV); Si (1619 eV); Br (1396 eV); I (511 and 520 eV); and Pt (1967 eV).

Results and Discussion

a. Correlation of Auger Spectroscopic and Electrochemical Analysis of Electrostatically Bound Anions: Binding of $IrCl_6^{2-}$. Pt electrodes bearing $\sim 10^{-8}$ mol/cm$^2$ of $(PQ^{2+}.2Br^-)$ exhibit essentially reversible reduction of the $(PQ^{2+})_n$ at -0.5 V vs. SCE in 0.1 M $K_2SO_4$ solution. If $K_2IrCl_6$ is introduced into the solution an additional redox system is detectable by cyclic voltammetry at ~+0.6 V vs. SCE that is attributable to the $IrCl_6^{2-/3-}$ redox couple. At concentrations of $IrCl_6^{2-}$ where no $IrCl_6^{2-/3-}$ cyclic voltammetry wave is detectable for a naked electrode (1-50 μM) we observe a wave for electrodes bearing $\sim 10^{-8}$ mole/cm$^2$ of $PQ^{2+}$. We thus conclude, as was concludec previously for polyvinylpyridinium,[1-3] that the $(PQ^{2+})_n$ can electrostatically bind $IrCl_6^{2-}$ resulting in an electrochemical response that would otherwise be undetectable. Figure 1 shows cyclic voltammograms for five different electrodes bearing about the same amount of $(PQ^{2+})_n$ in 0.1 M $K_2SO_4$ solution but with a different concentration of $IrCl_6^{2-}$ in solution in each case. The signal for $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ grows from zero to the value shown in 10-15 min. The data in Figure 1 are representative for this system and are believed to reflect the equilibrium amount of $IrCl_6^{3-}$ electrostatically bound in $(PQ^{2+})_n$. While $IrCl_6^{2-}$ is present in the bulk, the species actually bound is $IrCl_6^{3-}$ because the electrodes were held at a potential sufficiently negative to reduce the $IrCl_6^{2-}$. Thus, equation (4) represents the ion

$$\text{surface-}(PQ^{2+}.SO_4^{2-})_n + \tfrac{2}{3}xnIrCl_6^{3-} \rightleftarrows \text{surface-}(PQ^{2+}.\tfrac{2}{3}xIrCl_6^{3-} + (1-x)SO_4^{2-})_n + xnSO_4^{2-} \quad (4)$$

exchange reaction. By integrating the cyclic voltammetry waves the value of x is determined to vary from ~0.1 up to ~1.0, Table I, depending on the bulk concentration of $IrCl_6^{2-}$. At very low concentrations of $IrCl_6^{2-}$ there might be some concern as to whether there is significant depletion of the bulk $IrCl_6^{2-}$. For ~25 ml solutions of the 1 μM $IrCl_6^{2-}$ there is a total reservoir of ~25 nmoles of $IrCl_6^{2-}$; for x = 1.0 this would represent a diminution in the reservoir of $IrCl_6^{2-}$ by less than 25%, since the electrode bears only 7.6 nmoles of $PQ^{2+}$. That the amount of $IrCl_6^{3-}$ in the electrode is the equilibrium amount is established by showing

that an electrode where x = 1.0 initially changes in time to a value consistent with the bulk $IrCl_6^{2-}$ concentration associated with the solution contacting the electrode. Thus, the same eventual amount of $IrCl_6$ attained at given bulk concentration of $IrCl_6^{2-}$, independent of the initial value of x, for a fixed $K_2SO_4$ concentration. The timescale of the equilibration, however, can be quite long, requiring >15 min. in some cases.

Two, more subtle,observations tend to confirm the conclusion that $SO_4^{2-}/IrCl_6^{2-/3-}$ equilibration does occur. First, note that $IrCl_6^{2-}$ can be introduced as the 2- species by not potentiostatting the electrode. In the 50 μM $IrCl_6^{2-}$ solution we find that the area under the wave for $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ is initially very close to that under the wave for $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$, when the non-potentiostatted electrode is equilibrated with the solution. However, holding the electrode between $E°(PQ^{2+/+\cdot})_n$ and $E°(IrCl_6^{2-/3-})$ for a few minutes and then scanning to determine the amount of surface-confined $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ reveals a diminution in the area under the wave for $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ to a value consistent with the binding of $IrCl_6^{3-}$ to an extent that the positive charge of the $(PQ^{2+})_n$ is fully compensated. It is reasonable that if $IrCl_6^{2-}$ is bound to the fullest extent at 50 μM then $IrCl_6^{3-}$ would be bound just as well, if not better, since it bears a higher negative charge. The second observation concerns the effect from putting a $Pt/(PQ^{2+} \cdot \frac{2}{3}IrCl_6^{3-})_n$ electrode at a potential of ~-0.65 V vs. SCE, where the surface-$(PQ^{2+})_n$ is put in the reduced state $(PQ^{+\cdot})_n$, in a solution containing 50 μM $IrCl_6^{2-}$. The first several scans to determine surface $IrCl_6^{3-}$ show the approximately 50% diminution of the signal for $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ expected from the reduction in positive charge of the polymer. These two experiments show that $IrCl_6^{2-/3-}$ can move in and out of the $(PQ^{2+})_n$ layer with sufficient facility that equilibrium with the solution ions can be established.

Two additional points should be made here. First, the cyclic voltammetry is not useful in establishing whether there is additional electrolyte in the surface layer beyond that associated with charge compensation of the $(PQ^{2+})_n$. For example, there may be $K_2SO_4$ present in the polymer layer. Since reasonable electrochemical responses are observed for the $(PQ^{2+/+\cdot})_n$ and for surface-confined $IrCl_6^{2-/3-}$, the presence of $H_2O$ in the polymer layer is certain. But whether $K_2SO_4$ is present in the layer is unclear. It is unlikely that excess electrolyte can be excluded, and indeed it may be that $K^+$ and $SO_4^{2-}$ are the most mobile ions when there is as much $IrCl_6^{2-/3-}$ as $PQ^{2+}$ in the polymer layer. In any event, the local concentration of ions in the polymer layer far exceeds the bulk concentration even when the bulk concentration of electrolyte is 0.1 M. In the absence of a firmly bound anion such as $IrCl_6^{3-}$, the supporting electrolyte charge compensates the polymer thereby enhancing the electrolyte concentration near the electrode. When a firmly bound anion is present the concentration of supporting electrolyte may in fact be smaller than in solution, but the total ion concentration in the region near the electrode is always higher when the polymer is present. The second point of importance is that the extent to which $IrCl_6^{2-/3-}$ will be present in the surface polymer depends on the other ions present in the solution. This will be elaborated more fully below but it should be noted here that there are more and less competitive anions than $SO_4^{2-}$.

The electrodes characterized by the data in Figure 1 and Table I were studied further by Auger spectroscopy, to establish a quantitative correlation between the electrochemically detected $IrCl_6^{2-/3-}$ and Auger signals characteristic of the $IrCl_6^{2-/3-}$. Electrodes were removed from the solutions containing the various $IrCl_6^{2-}$ concentrations and washed with distilled, deionized $H_2O$. The five electrodes having variable $IrCl_6^{3-}$ content presumably have the surface$(PQ^{2+} \cdot \frac{2}{3}xIrCl_6^{3-} \cdot (1-x)SO_4^{2-})$ composition present

in the electrolyte solution from which each was withdrawn, except for the complication of the unknown $K_2SO_4$ content. The Auger spectra of the electrodes show signals for C, N, Si, and O, that are expected for $(PQ^{2+})_n$, Figure 2, and additional signals are present in the spectrum that are attributable to the elements S (from $SO_4^{2-}$) and Ir and Cl (from $IrCl_6^{3-}$) depending on the solution from which the surface is withdrawn. No additional signals are observed, and in particular, we find little or no detectable signal for K (252 eV) (from $K^+$). Any $K_2SO_4$ in the polymer is likely washed away during rinsing with $H_2O$ following removal from the $K_2IrCl_6/K_2SO_4$ solution. For each electrode the ratio of the N signal to the C signal is the same, $\pm$20%, but the Cl to C ratio varies in a smooth fashion depending on the concentration of $IrCl_6^{2-}$ in the solution from which the electrode was withdrawn, Figure 3. The correlation in Figure 3 is also with the data in Figure 1 that gives the ratio of electroactive, surface-confined $PQ^{2+/+\cdot}$ and $IrCl_6^{2-/3-}$. As shown in Figure 3 there is excellent internal consistency between the in situ electrochemical determination of $IrCl_6^{2-/3-}$ and the Auger determination of a washed and dried surface taken from the electrolyte solution. Thus, we can associate particular Cl/C ratios from Auger with a particular fractional incorporation of electroactive $IrCl_6^{3-/2-}$.

In our earlier work[11] we showed by Auger that the replacement of $Br^-$ by $Cl^-$ according to equation (5) occurs to an extent that no $Br^-$ is detectable

$$(PQ^{2+}.2Br^-)_n \xrightarrow[\text{Aqueous KCl}]{} (PQ^{2+}.2Cl^-)_n + 2nKBr \qquad (5)$$

by Auger spectroscopy. For such a surface the Cl/C ratio is less than for $(PQ^{2+}.PtCl_6^{2-})_n$ by an amount that about reflects the factor of three lower Cl content. The Cl/C ratio for an electrode prepared according to equation (6) likewise is about a factor of three greater than for

$$(PQ^{2+}.2Br^-)_n \xrightarrow[5\ \text{mM}\ K_2IrCl_6]{} (PQ^{2+}.IrCl_6^{2-})_n + 2nKBr \qquad (6)$$

surface-$(PQ^{2+}.2Cl^-)_n$. The difference with the $IrCl_6^{2-}$ is that we can know the amount of electroactive $IrCl_6^{2-/3-}$ that is present, in contrast to $PtCl_6^{2-}$

which does not exhibit reversible electrochemistry. Since the $IrCl_6^{2-}$ is very similar to $PtCl_6^{2-}$ in size and charge, the behavior of $IrCl_6^{2-}$ is expected to be close to that for $PtCl_6^{2-}$ in terms of incorporation into $(PQ^{2+})_n$ when competing against other anions.

Auger spectroscopic analysis of electrode surfaces bearing $(PQ^{2+})_n$ and the charge compensating anions reveal the surfaces to be reasonably free of detectable contaminants. At least we do not observe signals for extraneous elements and the elements that are expected to be present are detectable. One additional check of internal consistency comes from monitoring the Auger signal intensity for the various detectable elements while sputtering away the exposed surface with a beam of reactive Ar ions. This so-called depth profile analysis gives information concerning the elemental composition of the electrode/polymer interface as a function of depth in the polymer. A typical set of depth profile analyses are given in Figure 4. Note that substrate Pt signals overlap those for N; Si and N are low sensitivity elements. These facts account for the nearly independent signal intensity for N and Si as a function of sputtering time. Generally, there is some variation in element ratios near the surface, as detected by the changing Auger signal intensity as the sputtering time increases. But within a short time, it would appear that the polymer layer, bearing different anions, does have constant composition. The Auger signal intensities without sputtering may thus be suspect, since these may not always accurately reflect the composition of the bulk of the polymer. On the other hand, the sputtering technique itself is a destructive one and can lead to selective removal of various substances as the surface suffers damage from both the Auger exciting beam and the Ar ion sputtering beam.[16] We generally find good qualitative agreement for Auger with and without sputtering in the sense that selective anion binding can be determined to occur, Figures 2 and 4. However, as is well appreciated by other workers using Auger spectroscopy, the quantitative determination of element ratios by Auger spectroscopy will not be as good as an elemental analysis from combustion analyses. We find very reasonable reproducibility and would

estimate an error of less than ±30% in determining the ratio of compensating anions in $(PQ^{2+})_n$ when taking ratios from depth profile analyses.

b. Electrostatic Binding of Electroactive Transition Metal Cyanide Complexes. The incorporation of the electroactive $IrCl_6^{2-/3-}$ system into $(PQ^{2+})_n$ prompted us to examine the electrostatic binding of other negatively charged metal complexes. One large class of such complexes are the transition metal cyanides, a number of which can in fact be isolated in at least two oxidation states. We have thus examined the behavior of $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$ as representative of this class. Of these, only $Co(CN)_6^{3-}$ does not exhibit reversible electrochemical behavior.

The metal cyanide complexes bind strongly to the $(PQ^{2+})_n$. Figure 5 shows typical electrochemical behavior of Pt electrodes derivatized with I before and after incorporation of $Fe(CN)_6^{4-}$ or $Mo(CN)_8^{4-}$. Incorporation of the metal complex was brought about by dipping the unpotentiostatted $(PQ^{2+}\cdot 2Br^-)_n$ coated electrodes into an aqueous ~5 mM solution of the appropriate complex as the $K^+$ salt for ~5 min. The electrode was then removed, washed, and re-examined by cyclic voltammetry in 0.1 M KCl to determine whether any electroactive complex was retained. As shown in Figure 4 cyclic voltammetry waves having an area of ~½ of that for the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ are initially observed after replacement of $Cl^-$ by $Mo(CN)_8^{4-}$ or $Fe(CN)_6^{4-}$. This ~1:2 ratio is that expected for complete compensation of charge by the complexes. The waves for the electrostatically bound anions do diminish with time in 0.1 M KCl, but even after 4 h detectable waves still obtain. For finite volumes of electrolyte solution it is apparent that there can be measurable amounts of the complex anions that persist in the polymer at equilibrium.

As for electrodes bearing $(PQ^{2+})_n$ into which $IrCl_6^{2-}$ is incorporated, Figure 4, we have recorded Auger spectra for unpotentiostatted Pt electrodes bearing $(PQ^{2+})_n$ that have been withdrawn, and subsequently washed, from solutions containing variable amounts of $K_4Fe(CN)_6$ and a fixed concentration of KCl. Auger spectra for a pair of electrodes are given in Figure 6. As expected, the Cl

signal associated with the $(PQ^{2+}.2Cl^{-})_n$ is attenuated for the electrode withdrawn from the solution containing the higher $Fe(CN)_6^{4-}$ concentration. When incorporated, Figure 6b, $Fe(CN)_6^{4-}$ bound to the $(PQ^{2+})_n$ exhibits a signal characteristic of Fe. Moreover, there is a definite change in the ratio of the C/N ratio in accord with a high relative N concentration in $(PQ^{2+}.\frac{1}{2}Fe(CN)_6^{4-})_n$ compared to $(PQ^{2+}.2Cl^{-})_n$. The data in Figure 6 provide further substantiation of the Auger spectroscopic technique as a method to determine the relative binding of one anion compared to another. For all of the transition metal complexes that we have investigated, $MCl_6^{2-}$ (M = Pt, Ir); $M(CN)_z^{n-}$ (M = Co, Fe, Ru, Mo), we find that only small concentrations are required to completely displace the small inorganic anions such as $X^-$ (X = Cl, Br, I, NCS, $ClO_4$) or $SO_4^{2-}$ from the $(PQ^{2+})_n$ on the surface, even when the small anions are present at significant (~0.1 M) bulk concentration. Auger and electrochemical measurements have been employed to draw this conclusion. In the sections c. and d. below, we detail the procedures for ordering the binding of the anions.

The metal cyanides studied are not substitution labile and likely remain intact upon binding to the $(PQ^{2+})_n$. We find that in aqueous 0.1 M KCl the positions of the cyclic voltammetry waves are close to those found when the complexes are examined at the naked electrode surfaces, Table II. Thus, like the $IrCl_6^{2-/3-}$ system, the metal cyanides can be incorporated into the polymer

with relatively little perturbation of the electrochemistry. The kinetics for the surface-confined species have not been studied in detail, but Figure 7 shows the variation of the cyclic voltammograms for electrostatically bound $Mo(CN)_8^{4-}$, illustrating that the $Mo(CN)_8^{3-} \rightleftarrows Mo(CN)_8^{4-}$ process is sufficiently fast to give the expected linear response of peak current with scan rate up to 200 mV/s. Data represented by Figure 7 for $Mo(CN)_8^{3-/4-}$ are representative of that for the other electrostatically bound anions that are electroactive.

The effect of the anion on the electrochemical response of the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ system is quite noticeable, Figure 5. The tightly bound anions ($Co(CN)_6^{3-}$, $Fe(CN)_6^{3-/4-}$, $Ru(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, and $IrCl_6^{2-/3-}$) tend to broaden the wave and shift the average position of the oxidation and reduction current peaks to somewhat more negative potentials. The kinetics for the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ are also worsened by the incorporation of the tightly bound anions as reflected in the appearance of the cyclic voltammograms at scan rates exceeding 100 mV/s: the peak-to-peak separation increases and the waves appear broader. It is interesting that the electrochemical response of the metal complex is as good as it is, while the kinetics of the $(PQ^{2+})_n$ system suffer upon incorporation of the anion.

The electrochemical behavior of Pt electrodes bearing species such as $(PQ^{2+}.\frac{1}{2}Fe(CN)_6^{4-})_n$ is, not unexpectedly, dependent on the solvent. Since $E°(Fe(CN)_6^{3-/4-})$ is dependent on solvent,[17] we felt that this sensitivity to solvent could be exploited to reveal the solvent composition inside the polymer layer compared to the bulk. Changing the solvent from $H_2O$ to $CH_3CN$ does have a profound effect on <u>both</u> the behavior of the $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ and $Fe(CN)_6^{3-} \rightleftarrows Fe(CN)_6^{4-}$ systems. The $Fe(CN)_6^{3-/4-}$ wave is shifted more negative, broadened, and like the $(PQ^{2+/+\cdot})_n$ wave appears to be reduced in total area. Similar effects are found for the $(PQ^{2+}.\frac{1}{2}Mo(CN)_8^{4-})_n$. The poor electrochemical response in $CH_3CN$ is found with 0.1 <u>M</u> $[\underline{n}\text{-}Bu_4N]ClO_4$, $LiClO_4$, or $[Et_4N]Cl$ as supporting electrolyte. In all cases it would appear that the solvation by $CH_3CN$ is so poor that the electrochemical behavior

of the surface groups is drastically worse. Changing from $H_2O$ to $CH_3CN$ solvent for a system such as $(PQ^{2+}.2Cl^-)_n$ on Pt only modestly affects the electrochemical response of the $(PQ^{2+/+\cdot})_n$ at cyclic voltammetry scan rates of ~100 mV/s. It would thus appear that the deleterious effects from $CH_3CN$ as solvent can be attributed to the tight ion pairing of $(PQ^{2+})_n$ with the large anionic complexes. Interestingly, it would appear that only small amounts of $H_2O$ added to $CH_3CN$ (<5% by volume) are required to essentially regenerate the electrochemical properties found in pure $H_2O$ solvent. The $(PQ^{2+}.\text{complex anion})_n$ may concentrate the $H_2O$ beyond the bulk concentration, since $H_2O$ may solvate the ion pairs much more strongly.

Since the complex anions are persistently electrostatically bound to $(PQ^{2+})_n$ in solutions of 0.1 M KCl that contain no added complex anion, it is logical to conclude that the rate of loss of the complex is slow and that there is only slow movement of the complex anions in and out of the $(PQ^{2+})_n$ as the electrode is cycled between $(PQ^{2+})_n$ and $(PQ^{+\cdot})_n$. In these situations the essential charge neutrality of the polymer layer must be brought about by the movement of the cations, say $K^+$, in and out of the layer. Thus, relatively fast $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ interconversion or redox cycling of the complex anion may depend on the cation mobility when there are complex anions tightly bound to the $(PQ^{2+/+\cdot})_n$ layer. As for $IrCl_6^{2-/3-}$, though, holding the polymer layer in the reduced state, $(PQ^{+\cdot})_n$, will result in the eventual extrusion of the proper fraction of complex anion. A saturated solution of KCl will more rapidly lead to the dimunition of the electrochemical response of the electrostatically bound anion.

c. Ordering the Binding of Complex Anions. As indicated above, the transition metal complex anions are much more firmly bound than the simple inorganic anions. In this section we describe results establishing the relative ordering of complex anion binding to $(PQ^{2+})_n$. To illustrate the issue we can ask whether $IrCl_6^{2-}$ or $Fe(CN)_6^{4-}$ will be the charge compensating ion for $(PQ^{2+})_n$ when the solution contains both $IrCl_6^{2-}$ and $Fe(CN)_6^{4-}$. To answer such a question we exploit the fact that both ions are reversibly electroactive and examine the electrochemical response of a $(PQ^{2+})_n$-coated Pt electrode in a solution containing 0.1 M KCl, 50 μM $K_2IrCl_6$ and 50 μM $K_4Fe(CN)_6$. The potential range scanned is such that $(PQ^{2+})_n$ remains in the oxidized (2+) state. Initially, cyclic voltammetry waves are observed for the $Fe(CN)_6^{3-} \rightleftarrows Fe(CN)_6^{4-}$ and for the $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ systems. However, eventually the signal for the Ir system vanishes while the signal for the Fe system increases until the cyclic voltammetry shows that the charge associated with $(PQ^{2+})_n$ is completely neutralized by the electroactive $Fe(CN)_6^{4-}$. Thus, we conclude that both $IrCl_6^{2-}$ and $Fe(CN)_6^{4-}$ can quickly go into the polymer, but the thermodynamics are such that $Fe(CN)_6^{4-}$ is significantly more firmly bound. Likewise, examining the electrochemical response of a $(PQ^{2+})_n$-coated electrode after ~15 min equilibration in 0.1 M KCl, 50 μM $K_2IrCl_6$, and 50 μM $K_4Fe(CN)_6$ shows waves for only the $Fe(CN)_6^{3-/4-}$ couple.

Examination of the electrochemical response of a $(PQ^{2+})_n$-coated Pt electrode in 0.1 M KCl, 50 μM $K_4Fe(CN)_6$, 50 μM $K_4Mo(CN)_8$ initially reveals cyclic voltammetry signals for both the Fe and Mo systems. During the first few cyclic voltammetry scans the signal for the Fe and the Mo systems both grow, but the signal for Fe grows faster. This suggests that the $Fe(CN)_6^{4-}$ is more mobile than $Mo(CN)_8^{4-}$. Eventually, the signal for the Fe system declines while the Mo signal slowly grows to reflect a very high $Mo(CN)_8^{4-}/Fe(CN)_6^{4-}$ ratio bound to $(PQ^{2+})_n$. Similar experimentation shows that $Mo(CN)_8^{4-}$ is bound much more firmly than $Ru(CN)_6^{4-}$, while $Ru(CN)_6^{4-}$ is only slightly more firmly bound than $Fe(CN)_6^{4-}$.

The results from cyclic voltammetry of $(PQ^{2+})$-coated Pt electrodes in the presence of pairs of the electroactive complex anions allows us to establish the ordering of binding:

$$Mo(CN)_8^{4-} > Ru(CN)_6^{4-} \sim Fe(CN)_6^{4-} > IrCl_6^{2-/3-} >> Cl^-$$

$$\longleftarrow$$
Increased Binding

Attenuation of the cyclic voltammetry wave for polymer-bound $Fe(CN)_6^{3-} \rightleftarrows Fe(CN)_6^{4-}$ by adding $K_3Co(CN)_6$ to a solution of 0.1 M KCl/50 μM $K_4Fe(CN)_6$ provides evidence for the strong and competitive binding of $Co(CN)_6^{3-}$ even though $Co(CN)_6^{3-}$ is electrochemically silent in the accessible potential range in $H_2O$. For example, addition of $K_3Co(CN)_6$ to bring its concentration to 25 μM attenuates the signal for the $Fe(CN)_6^{3-/4-}$ couple to ~50% of its initial value; addition of $K_3Co(CN)_6$ to a concentration of 50 μM attenuates the wave for $Fe(CN)_6^{3-/4-}$ even more, to about 30% of its original value. These experiments place $Co(CN)_6^{3-}$ in the vicinity of $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$. However, $Co(CN)_6^{3-}$ is considerably more weakly bound than $Mo(CN)_8^{4-}$. This conclusion follows from the fact that $Mo(CN)_8^{4-}$ is the dominant polymer-bound electroactive ion when $(PQ^{2+})_n$-coated Pt electrodes are immersed in electrolyte solutions containing equal concentrations of $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$, whereas $Fe(CN)_6^{4-}$ is still present at significant concentration in the $(PQ^{2+})_n$ when $Fe(CN)_6^{4-}$ and $Co(CN)_6^{3-}$ are in the bulk solution at equal concentration.

The same signal for the $Fe(CN)_6^{3-/4-}$ system is eventually observed if a $(PQ^{2+}.2Cl^-)_n$-coated electrode is immersed into a 0.1 M KCl solution that contains 50 μM $K_4Fe(CN)_6$ and 50 μM $K_3Co(CN)_6$ as when a $(PQ^{2+}.\frac{1}{2}Fe(CN)_6^{4-})_n$ electrode is immersed into the same solution. The point is that the composition of the surface-bound polymer·anion system, $(PQ^{2+}.xFe(CN)_6^{4-}.yCo(CN)_6^{3-})_n$, is obtained independent of the initial composition of the electrode or the order of addition of reagents. The conclusion is that the $(PQ^{2+})_n$-coated Pt does come

into equilibrium with the ions in solution. Similarly, concerning the composition of the bound, electroactive anions $M(CN)_6^{4-}$ (M = Fe, Ru); $Mo(CN)_8^{4-}$; and $IrCl_6^{2-}$ the electrochemical response is eventually independent of the initial distribution of ions in the polymer, and the order of addition of anions to a solution does not alter the distribution of detected anions in the $(PQ^{2+})_n$ layer. Thus, in all cases, our measurements of anion binding are for situations where we are certain that equilibrium has been established; we are not limited by kinetically sluggish ion exchange. Table III summarizes the experimentation discussed so far to establish the ordering of the binding of complex anions, and Figures 8 and 9 illustrate typical cyclic voltammetry data for such experimentation. Comparison of wave shapes in Figures 1, 5, 7-9 indicate considerable variation. Such variation may be due to the differences in coverage, degree of cross-linking in the polymer, and the nature of the distribution of electroactive complex(es) present in the film.

Auger spectroscopy can also be used to order the binding of the tightly bound transition metal complexes, as illustrated by the spectra given in Figures 2 and 6. Generally, the unique Auger signal for the metal ion of the complex is weak and element ratios are not always easily quantitated. For example, the signal for Fe or Mo when the respective cyanide complexes are bound to $(PQ^{2+})_n$ is very weak relative to the signal for C. Consequently, we have not used Auger to order binding of the tightly bound, electroactive metal complexes.

d. Ordering the Binding of Weakly Bound, Non-Electroactive Anions. Table IV details Auger spectroscopy results that allow us to order the binding of several anions to the $(PQ^{2+})_n$. A typical experiment involves dipping a $Pt/(PQ^{2+}\cdot 2Br^-)_n$ electrode into an aqueous solution containing a one-to-one ratio of two anions. Equilibration at 25°C for 15 min is generally sufficient to insure that the anions in the polymer reflect the equilibrium situation. The equilibrated surface is then removed from the solution, washed with distilled $H_2O$, and then analyzed for the anion by Auger/depth profile analysis.

The series of experiments summarized by the data in Table IV allow the ordering of anions:

$$I^- > SCN^- \sim ClO_4^- \sim SO_4^{2-} > Br^- > Cl^- \sim \underline{p}\text{-toluenesulfonate}$$
$$\xleftarrow[\text{increasing binding}]{}$$

All of the transition metal complex anions are much more firmly bound than these anions. The relative binding spans a range of only about a factor of ten from $I^-$ to $Cl^-$ in the sense that a solution containing ~10/1 $Cl^-/I^-$ will give a polymer having a ~1/1 $Cl^-/I^-$. In the same sense, $IrCl_6^{2-}$ to $SO_4^{2-}$ spans a range of $10^3$-$10^4$ in that ~20 $\mu\underline{M}$ $K_2IrCl_6$/0.1 $\underline{M}$ $K_2SO_4$ yields a polymer having ~1/1 $SO_4^{2-}/IrCl_6^{2-}$.

Given the results of others concerning the electrostatic binding of transition metal complexes to surface-confined polyions, the rather strong binding of the transition metal complexes to $(PQ^{2+})_n$ is not surprising.[1-3] For the weakly bound ions we find that the ions are very labile. Even the strongest of the weakest surface-confined ions, $I^-$ is labile. Cyclic voltammetry signals apparently associated with $3I^- \rightleftarrows I_3^-$ for $Pt/(PQ^{2+}.2I^-)_n$ electrodes immersed in 0.1 $\underline{M}$ KCl last for only a few scans at 100 mV/s, whereas the tightly bound metal complexes give rise to persistent cyclic voltammetry signals. The cyclic voltammetry (100 mV/s) for $(PQ^{2+/+\cdot})_n$ is not significantly dependent on the supporting electrolyte (0.1 $\underline{M}$) when a weakly bound anion is used. Thus, a wide range of $K^+$ or $Na^+$ salts are useful as the electrolyte for the $(PQ^{2+/+\cdot})_n$-coated electrodes. Only when the anion is strongly bound do we observe adverse effects on the kinetics of the $(PQ^{2+/+\cdot})_n$ redox system.

Summary

Electrochemical and Auger spectroscopic data establish a wide range of relative binding of anions to surfaces functionalized with $(PQ^{2+})_n$. Large, substitution inert, anionic transition metal complexes such as $IrCl_6^{2-/3-}$, $Fe(CN)_6^{3-/4-}$, $Ru(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, and $Co(CN)_6^{3-}$ have all been found to be tightly bound against anions such as $I^-$, $Br^-$, $Cl^-$, $SCN^-$, $ClO_4^-$, $SO_4^{2-}$, or p-toluenesulfonate. The thermodynamically weakly bound anions are labile, rapidly displaced, and do not significantly alter the kinetics for the $(PQ^{2+/+\cdot})_n$ redox system. The strongly bound anions are not kinetically labile and do adversely affect the kinetics for the $(PQ^{2+/+\cdot})_n$ system. The correlation of the relative binding of $IrCl_6^{2-}$ vs. $SO_4^{2-}$ using electrochemical and Auger detection establishes Auger to be a reliable and useful technique to determine the surface elemental composition of electrode surfaces modified with the $(PQ^{2+})_n$ system. The electrochemical data support the conclusion that the capacity of the $(PQ^{2+})_n$-coated electrodes to bind transition metal complexes is determined by the number of $PQ^{2+}$ centers and the charge on the complex. Generally, complex anions can be bound to an extent that reflects complete charge compensation of the polyion bound to the surface. Finally, thermodynamics, not kinetics, has been shown to control the distribution of anions present in the surface bound $(PQ^{2+})_n$ when the electrolyte includes two or more anions.

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Table I. Concentration Dependence of Electrostatic Binding of $IrCl_6^{3-}$ to $Pt/(PQ^{2+}.\frac{2}{3}xIrCl_6^{3-} + (1-x)SO_4^{2-})_n$ in 0.1 M $K_2SO_4$.

| Electrode[a] | $[K_2IrCl_6]$[b] | $(PQ^{2+})_n \rightleftarrows (PQ^{+\cdot})_n$ | | $IrCl_6^{2-} \rightleftarrows IrCl_6^{3-}$ | | x |
|---|---|---|---|---|---|---|
| | | E°, V vs. SCE[c] | Coverage, mol/cm$^2$[d] | E°, V vs. SCE[c] | Coverage, mol/cm$^2$[d] | |
| (a) | 50 μM | -0.54 | $7.3 \times 10^{-9}$ | +0.66 | $5.1 \times 10^{-9}$ | 1.0 |
| | 0 | -0.51 | $7.3 \times 10^{-9}$ | --- | --- | 0.0 |
| (b) | 25 μM | -0.53 | $7.3 \times 10^{-9}$ | +0.66 | $3.9 \times 10^{-9}$ | 0.8 |
| | 0 | -0.51 | $7.3 \times 10^{-9}$ | --- | --- | 0.0 |
| (c) | 5.0 μM | -0.53 | $5.0 \times 10^{-9}$ | +0.68 | $1.8 \times 10^{-9}$ | 0.5 |
| | 0 | -0.51 | $5.0 \times 10^{-9}$ | --- | --- | 0.0 |
| (d) | 2.5 μM | -0.53 | $7.6 \times 10^{-9}$ | +0.69 | $1.1 \times 10^{-9}$ | 0.2 |
| | 0 | -0.51 | $7.6 \times 10^{-9}$ | --- | --- | 0.0 |
| (e) | 1.0 μM | -0.53 | $7.6 \times 10^{-9}$ | +0.68 | $0.5 \times 10^{-9}$ | 0.1 |
| | | -0.51 | $7.6 \times 10^{-9}$ | --- | --- | 0.0 |

[a] Electrodes (a)-(e) are those characterized by the cyclic voltammetry scans in Figure 1, (a)-(e), respectively. Each electrode is thus an independent experiment.

[b] Bulk solution (~25 ml) concentration.

[c] Average position of the oxidation and reduction current peak for the surface confined species.

[d] Coverage of electrochemically active material from integration of cyclic voltammetry wave divided by electrode area. Note that the $IrCl_6^{2-/3-}$ is actually bound as $IrCl_6^{3-}$ since the electrode is held between $E°(PQ^{2+/+\cdot})_n$ and $E°(IrCl_6^{2-/3-})$; cf. text. Coverages are ±10%; error is due to inability to accurately subtract background currents.

Table II. Electrochemical Potential of Aqueous and Electrostatically Bound Complex Anions.

| Complex | E°, V vs. SCE[a] | |
|---|---|---|
| | Solution | Bound to $(PQ^{2+})_n$ |
| $Fe(CN)_6^{3-/4-}$ | +0.19 ± 0.02 | +0.20 ± 0.03 |
| $Ru(CN)_6^{3-/4-}$ | +0.70 ± 0.02 | +0.68 ± 0.03 |
| $Mo(CN)_8^{3-/4-}$ | +0.57 ± 0.02 | +0.60 ± 0.03 |
| $IrCl_6^{2-/3-}$ | +0.65 ± 0.02 | +0.66 ± 0.03 |

[a]Electrochemical potentials, E°, for the indicated couple dissolved in $H_2O$ at 25°C or confined to $(PQ^{2+})_n$ measured for Pt electrodes in 0.1 M KCl by cyclic voltammetry. The E° is taken to be the average of the anodic and cathodic current peaks at a scan rate of 100 mV/s. The coverage of $(PQ^{2+})_n$ is generally in the range $5 \times 10^{-9}$ - $5 \times 10^{-8}$ mol/cm$^2$.

Table III. Electrochemical Experimentation to Establish Ordering of Binding of Complex Anions to $(PQ^{2+})_n$.

| Experiment # | Perturbation | Response | Conclusion |
|---|---|---|---|
| 1 | Dip $(PQ^{2+}.2Cl^-)_n$ electrode into 0.1 M KCl/50 μM $K_2IrCl_6$. | $(PQ^{2+/+\cdot})_n$ wave broadens and shifts negative; $IrCl_6^{2-/3-}$ wave grows in until equal in area of $(PQ^{2+/+\cdot})_n$. | $IrCl_6^{2-} >> Cl^-$ |
| 2 | Add $K_4Fe(CN)_6$ to 50 μM in above system. | $IrCl_6^{2-/3-}$ wave disappears; $Fe(CN)_6^{3-/4-}$ wave grows to ½ of $(PQ^{2+/+\cdot})_n$ wave. | $Fe(CN)_6^{4-} > IrCl_6^{2-}$ |
| 3 | Add $K_4Mo(CN)_8$ to 50 μM in above system. | $Fe(CN)_6^{3-/4-}$ wave disappears; $Mo(CN)_8^{3-/4-}$ wave appears and grows to ½ of $(PQ^{2+/+\cdot})_n$ waves. | $Mo(CN)_8^{4-} > Fe(CN)_6^{4-}$ |
| 4 | Add $K_4Ru(CN)_6$ to 50 μM in above system. | No change in cyclic voltammograms. | $Ru(CN)_6^{4-} < Mo(CN)_8^{4-}$ |
| 5 | Dip electrode from 4 into saturated KCl for 5 min and scan in 0.1 M KCl containing no other ions. | Original response of $(PQ^{2+/+\cdot})_n$ regenerated; no signals detectable for bound complexes. | $(PQ^{2+}.2Cl^-)_n$ regenerated by ion exchange with excess $Cl^-$. |
| 6 | Dip $(PQ^{2+}.2Cl^-)_n$ electrode into 0.1 M KCl/50 μM each of $K_4Fe(CN)_6$, $K_4Ru(CN)_6$, $K_2IrCl_6$, $K_4Mo(CN)_8$. | $(PQ^{2+/+\cdot})_n$ wave broadened and shifted negative; eventual growth of $Mo(CN)_8^{3-/4-}$ to an area of ½ of $(PQ^{2+/+\cdot})_n$ wave. | Binding of $Mo(CN)_8^{4-}$ unaffected by presence of other complexes. |
| 7 | Dip $(PQ^{2+}.2Cl^-)_n$ electrode into 0.1 M KCl/50 μM $K_2IrCl_6$/50 μM $K_4Fe(CN)_6$. | $(PQ^{2+/+\cdot})_n$ wave broadens and shifts negative; waves for $Fe(CN)_6^{3-/4-}$ and $IrCl_6^{2-/3-}$ initially grow; eventually wave for $IrCl_6^{2-/3-}$ vanishes and $Fe(CN)_6^{3-/4-}$ grows to ½ | Initial response kinetically controlled; eventual response thermodynamically controlled: $Fe(CN)_6^{4-} > IrCl_6^{2-}$ |

Table III. (Continued)

| Experiment # | Perturbation | Response | Conclusion |
|---|---|---|---|
| 8 | Dip $(PQ^{2+}\cdot\frac{1}{2}Fe(CN)_6^{4-})_n$ electrode into 0.1 M KCl/50 μM $K_4Fe(CN)_6$/50 μM $K_3Co(CN)_6$. | Wave for $Fe(CN)_6^{3-/4-}$ declines to a value reflecting 70% loss of $Fe(CN)_6^{3-/4-}$. | $Co(CN)_6^{3-} > Fe(CN)_6^{4-}$ |
| 9 | Dip $(PQ^{2+}\cdot 2Cl^-)_n$ electrode into 0.1 M KCl/50 μM $K_4Fe(CN)_6$. | $Fe(CN)_6^{3-/4-}$ wave grows to an area of ½ of that for $(PQ^{2+/+\cdot})_n$. $(PQ^{2+/+\cdot})_n$ wave broadens and shifts more negative. | $Fe(CN)_6^{4-} >> Cl^-$ |
| 10 | Dip $(PQ^{2+}\cdot 2Cl^-)_n$ electrode into 0.1 M KCl/50 μM $K_4Fe(CN)_6$/50 μM $K_3Co(CN)_6$. | Same cyclic voltammetry as in #8. | $Co(CN)_6^{3-} > Fe(CN)_6^{4-}$ |

Table IV. Auger Signal Intensities for Anions Bound in $(PQ^{2+})_n$.[a]

| Solution[b] | Signal Intensities, ±30%[c] | Conclusion |
|---|---|---|
| 0.1 M KCl | Cl/C = 0.67 | $Cl^-$ Bound |
| 0.01 M $K_2IrCl_6$ | Cl/C = 1.4 | $IrCl_6^{2-}$ Bound |
| 0.1 M KI | I/C ≈ 1.1 (O signal interferes)[d] | $I^-$ Bound |
| 0.10 M $K_2SO_4$ | S/C = 0.32 | $SO_4^{2-}$ Bound |
| 0.05 M Na[p-toluenesulfonate]<br>0.05 M KCl | S/C = 0.22; Cl/C = 0.20 | p-toluenesulfonate ≈ $Cl^-$ |
| 0.05 M KCl<br>0.05 M KBr | Br/C = 0.13; Cl/C = 0.09 | $Br^- > Cl^-$ |
| 0.05 M KCl<br>0.05 M KI | I/C ≈ 0.6[d]; Cl/C = 0.02 | $I^- > Br^- > Cl^-$ |
| 0.09 M KCl<br>0.01 M KI | I/C ≈ 0.5[d]; Cl/C = 0.28 | $I^- > Cl^-$ (factor of ~10) |
| 0.05 M KCl<br>0.05 M KSCN | S/C = 0.45; Cl/C = 0.02 | $SCN^- > Cl^-$ |
| 0.05 M KSCN<br>0.05 M KI | S/C = 0.29; I/C ≈ 0.3[d] | $SCN^- \approx I^-$ |
| 0.01 M KSCN<br>0.01 M $NaClO_4$ | S/C = 0.27; Cl/C = 0.59 | $ClO_4^- \approx SCN^-$ |
| 0.05 M KCl<br>0.05 M $K_2SO_4$ | S/C = 0.30; Cl/C = 0.04 | $SO_4^{2-} > Cl^-$ |
| 0.05 M KBr<br>0.05 M $K_2SO_4$ | S/C = 0.16; Br/C = 0.10 | $SO_4^{2-} \approx Br^-$ |
| 0.05 M KI<br>0.05 M $K_2SO_4$ | S/C = 0.05; I/C ≈ 0.6[d] | $I^- > SO_4^{2-}$ |

Table IV. (Continued)

| Solution[b] | Signal Intensities, ±30%[c] | Conclusion |
|---|---|---|
| 0.01 M $K_2SO_4$<br>0.01 M $NaClO_4$ | S/C = 0.16; Cl/C = 0.16 | $SO_4^{2-} \approx ClO_4^-$ |
| 1 mM $K_2SO_4$<br>1 mM $K_2PtCl_6$ [e] | S/C - noise[f]; Cl/C = 0.87 | $PtCl_6^{2-} >> SO_4^{2-}$ |
| 0.10 M $K_2SO_4$<br>50 μM $K_2IrCl_6$ [g] | S/C - noise[f]; Cl/C = 0.78 | $IrCl_6^{2-} >> SO_4^{2-}$ |

[a]Signal intensities (peak-to-peak height) are all relative to the C (272 eV) signal and are taken from depth profile analyses like those depicted in Figure 4. Data are from a portion of the depth profile where element ratios are the most constant.

[b]Aqueous solution (~25 ml) from which an electrode bearing $(PQ^{2+} \cdot 2Br^-)_n$ (coverage in the range $5 \times 10^{-9}$ to $5 \times 10^{-8}$ mol/cm$^2$) was withdrawn after equilibration for 15 min at 25°C.

[c]Signals given are only those characteristic of the anion. Except where noted, there was no interference in the energy window used in the depth profile.

[d]The I signal and O signal near 503 eV interfere, but when $I^-$ is present the signal in this energy range is larger. The $I^-$ signal is characteristic because it has two peaks, whereas the O signal has only one.

[e]These data were recorded using a 3 KeV electron beam; all other data were recorded using a 5 KeV electron beam. This may cause some variability in the element ratios.

[f]No signal beyond background was detectable.

[g]These data are from an Auger spectrum without sputtering, cf. Figure 2.

Figure Captions

Figure 1. Cyclic voltammograms (100 mV/s) of a Pt/$(PQ^{2+})_n$ electrode in solutions containing 0.1 M $K_2SO_4$ and (a) 50 μM $K_2IrCl_6$, (b) 25 μM $K_2IrCl_6$, (c) 5.0 μM $K_2IrCl_6$, (d) 7.5 M $K_2IrCl_6$, and (e) 1.0 μM $K_2IrCl_6$. The coverage of electroactive $(PQ^{2+/+\cdot})_n$ is $7.6 \times 10^{-9}$ moles/cm$^2$ for (a) and (b), $5.0 \times 10^{-9}$ moles/cm$^2$ for (c) and $7.3 \times 10^{-9}$ moles for (d) and (e). Cf. also Table I.

Figure 2. Auger spectra for Pt/$(PQ^{2+}\cdot\frac{2}{3} \times IrCl_6^{3-} + (1 - x)SO_4^{2-})_n$ electrodes. In (a) the electrode was withdrawn from a solution containing 0.1 M $K_2SO_4$ and 1 μM $K_2IrCl_6$ and is the electrode characterized by cyclic voltammetry in Figure 1e. In (b) the electrode was withdrawn from a solution containing 0.1 M $K_2SO_4$ and 50 μM $K_2IrCl_6$ and is the electrode characterized by cyclic voltammetry in Figure 1a. Each electrode was washed with $H_2O$ prior to the Auger and the surfaces were not sputtered. Note that the $IrCl_6^{3-}$, not $IrCl_6^{2-}$, is surface-confined, since the electrode was removed after electrochemical equilibration at a potential between $E°(PQ^{2+/+\cdot})_n$ and $E°(IrCl_6^{2-/3-})$.

Figure 3. A graph comparing electrochemical and Auger data for Pt/$(PQ^{2+}\cdot\frac{2}{3} \times IrCl_6^{3-} + (1-x)SO_4^{2-})_n$ electrodes. The cyclic voltammetry of these electrodes is shown in Figure 1. The scale on the left hand side refers to the ratio of the integrated areas of the $IrCl_6^{2-/3-}$ and $(PQ^{2+/+\cdot})_n$ waves, in solutions containing the appropriate concentration of $K_2IrCl_6$ (X). The scale on the right hand side refers to the ratio of Auger signals obtained for C and Cl on these same electrodes (●) without sputtering. Auger spectra for $[IrCl_6^{2-}]$ = 1 μM and 50 μM are shown in Figure 2. Auger signal intensities have not been corrected for element sensitivity.

Figure 4. Auger/depth profile analysis of $Pt/(PQ^{2+} \cdot xIrCl_6^{2-} + (1 - x)SO_4^{2-})_n$ electrodes. The electrode characterized in (a) was withdrawn from a solution of 5 mM $K_2IrCl_6$ and that in (b) was withdrawn from a solution of 0.1 M $K_2SO_4$. In (a) $x \simeq 1$ and in (b) $x \simeq 0$. Electrodes were washed with $H_2O$ prior to Auger analysis. Note that low energy Pt signals interfere with the low energy signals characteristic of other elements, especially S.

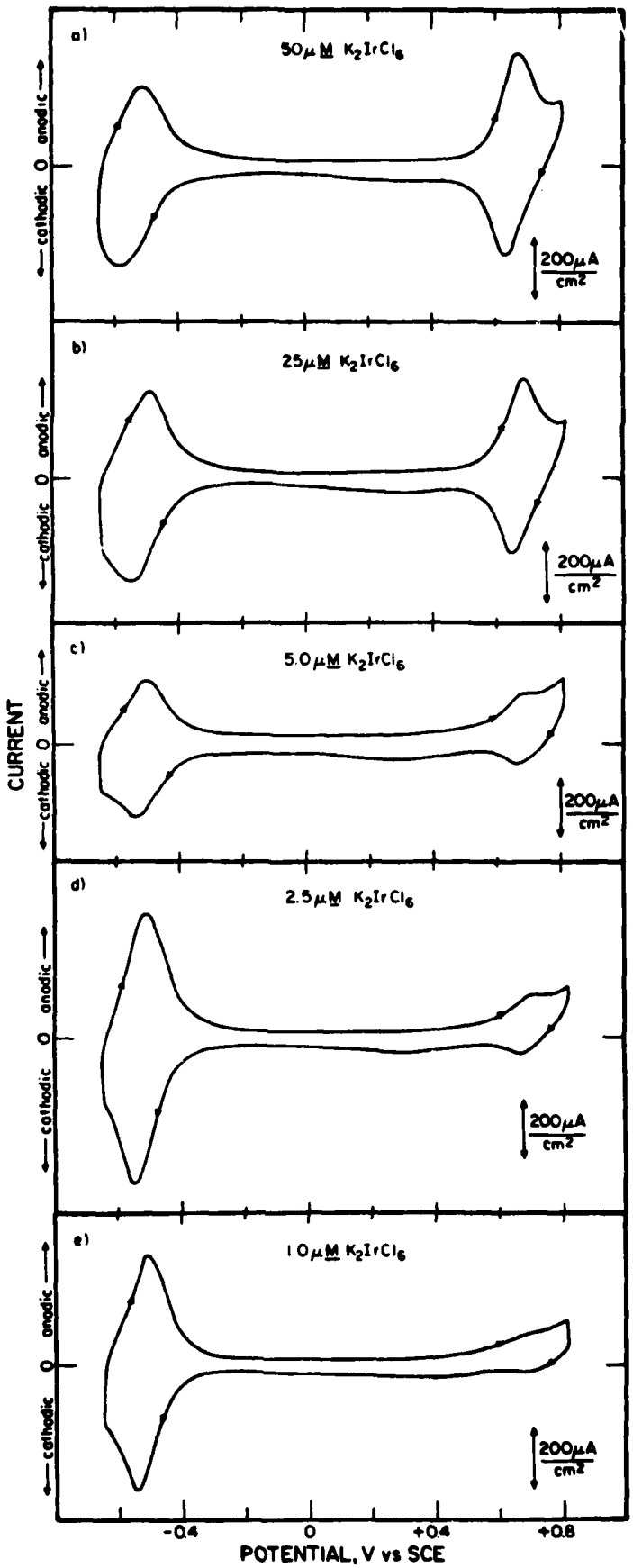
Figure 5. Cyclic voltammograms (100 mV/s) in 0.1 M KCl of electrode (a) a $Pt/(PQ^{2+} \cdot \frac{1}{2}Mo(CN)_8^{4-})_n$ electrode prepared by immersing a $Pt/(PQ^{2+})_n$ electrode into ~5 mM $K_4Mo(CN)_8/H_2O$, and then rinsing, and (b) at $Pt/(PQ^{2+} \cdot \frac{1}{2}Fe(CN)_6^{4-})_n$ electrode prepared as in (a) except using $K_4Fe(CN)_6$. The coverage of electroactive $(PQ^{2+/+})_n$ is $1.3 \times 10^{-8}$ mol/cm$^2$ for (a) and $3.7 \times 10^{-9}$ mol/cm$^2$ for (b).

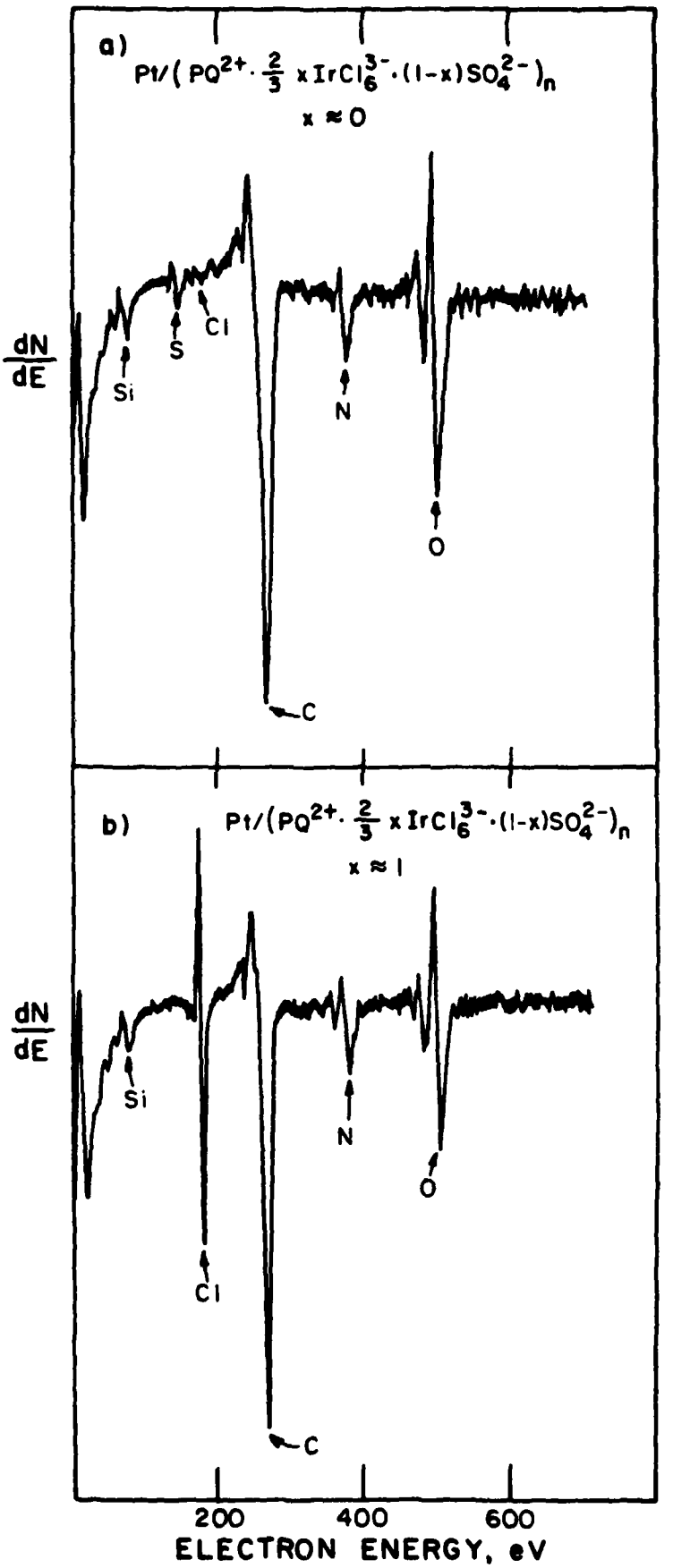
Figure 6. Auger spectral analysis of $Pt/PQ^{2+} \cdot 2xCl^- \cdot \frac{1}{2}(1 - x)Fe(CN)_6^{4-})_n$. In (a) the electrode was withdrawn from 0.1 M KCl, 1 μM $K_4Fe(CN)_6$; $x \simeq 1$ and in (b) the electrode was withdrawn from 0.1 M KCl, 100 μM $K_4Fe(CN)_6$; $x \simeq 0$. Electrodes were washed prior to Auger analysis but were not sputtered.

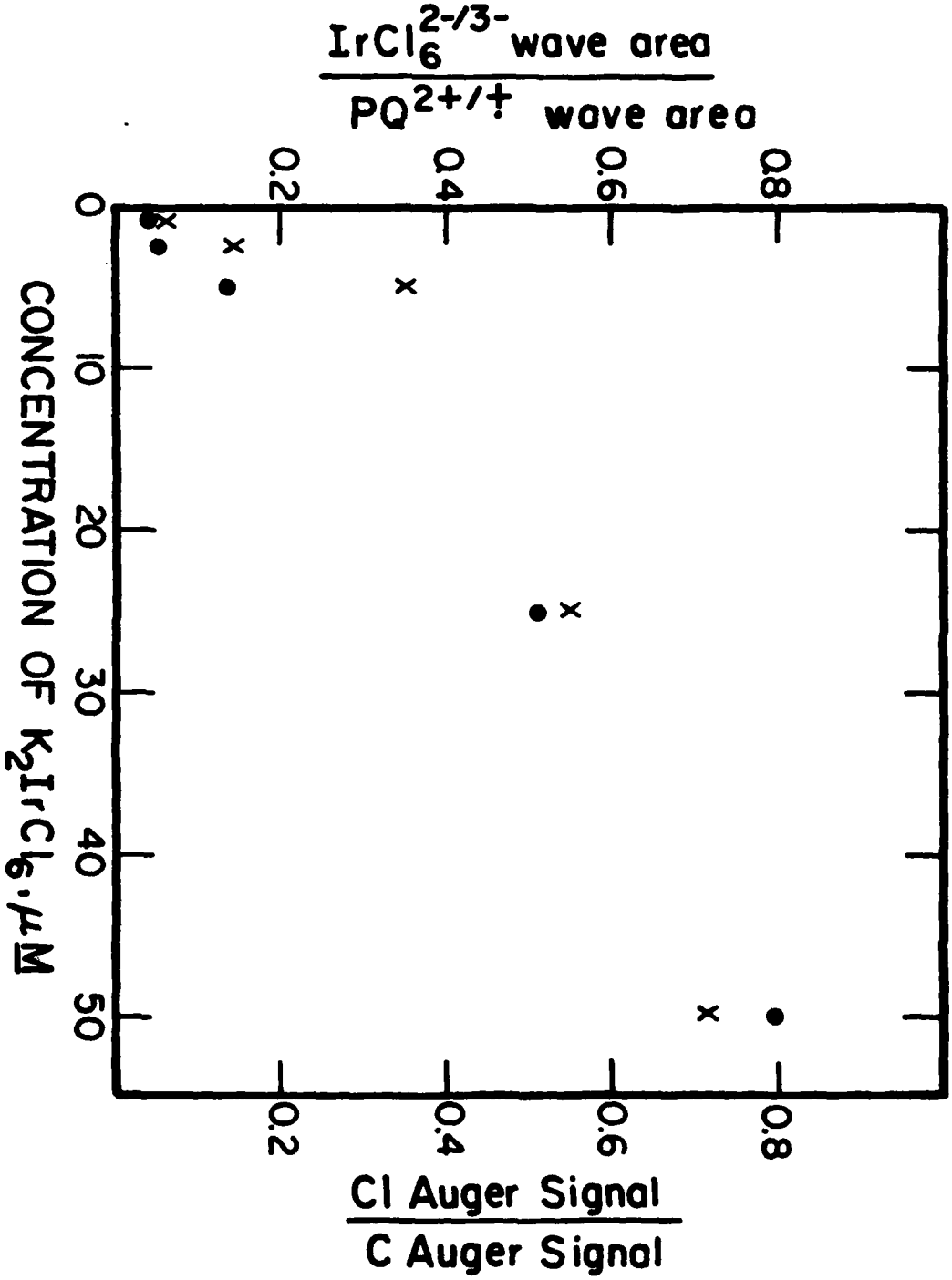
Figure 7. Cyclic voltammograms for a $Pt/(PQ^{2+} \cdot \frac{1}{2}Mo(CN)_8^{4-})_n$ electrode in 0.1 M $KCl/H_2O$ at different scan rates. The inset shows that the peak current for the $Mo(CN)_8^{4-/3-}$ wave varies linearly with the scan rate, as expected for a reversible, surface-attached species. The coverage of electroactive $(PQ^{2+})_n$ is $1 \times 10^{-9}$ mol/cm$^2$.

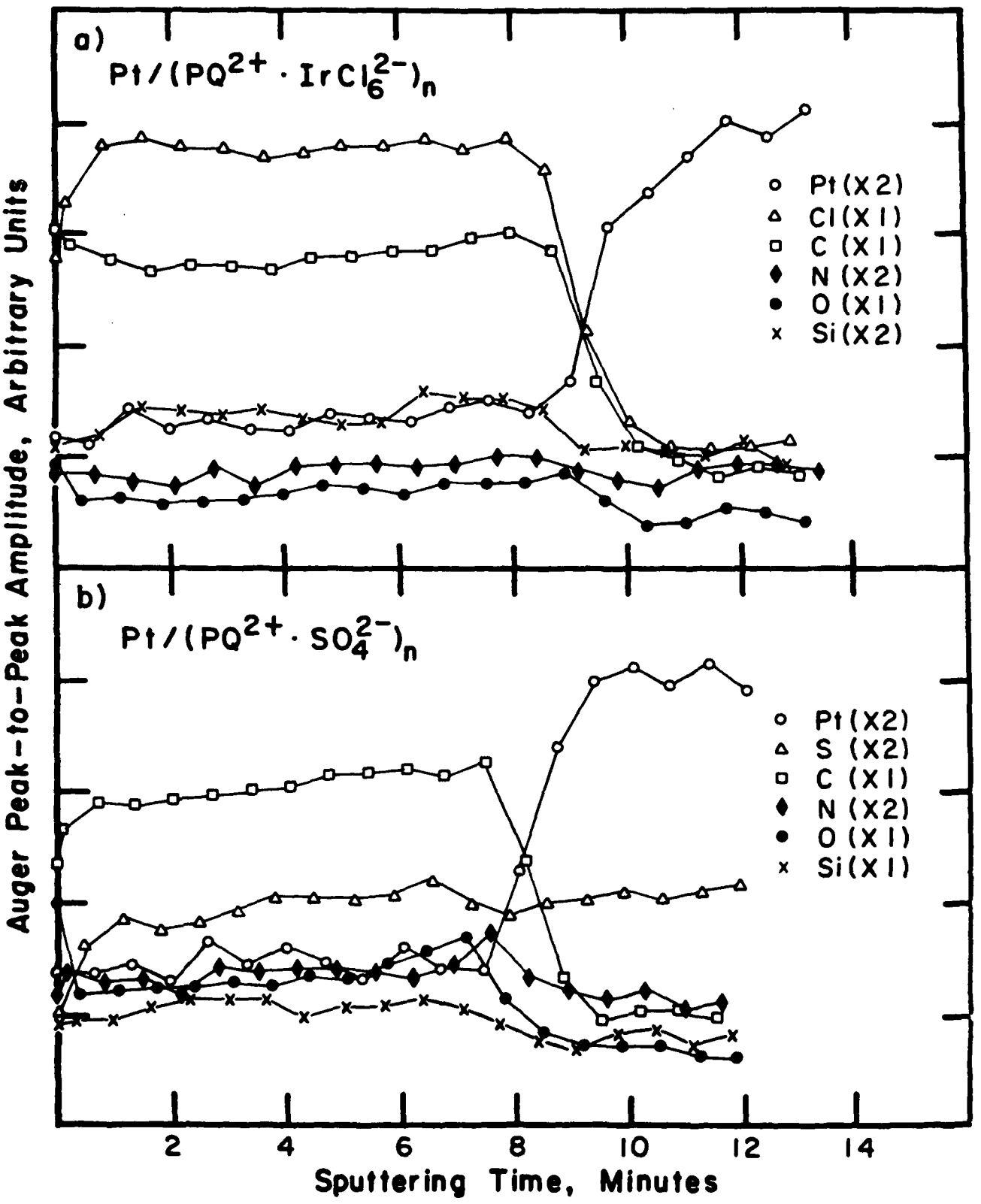
Figure 8. Cyclic voltammograms, 100 mV/s, of a $Pt/(PQ^{2+})_n$ electrode in (a) ---- 0.1 M KCl; —— 0.1 M KCl/50 μM $K_2IrCl_6$; (b) 0.1 M KCl/50 μM $K_2IrCl_6$/50 μM $K_4Fe(CN)_6$; (c) 0.1 M KCl/50 μM $K_2IrCl_6$/50 μM $K_4Fe(CN)_6$/50 μM $K_4Mo(CN)_8$. The coverage of $PQ^{2+}$ is $2.1 \times 10^{-8}$ mol/cm$^2$.
In each case the unpotentiostatted electrode was equilibrated for ~15 min prior to running the cyclic voltammogram.

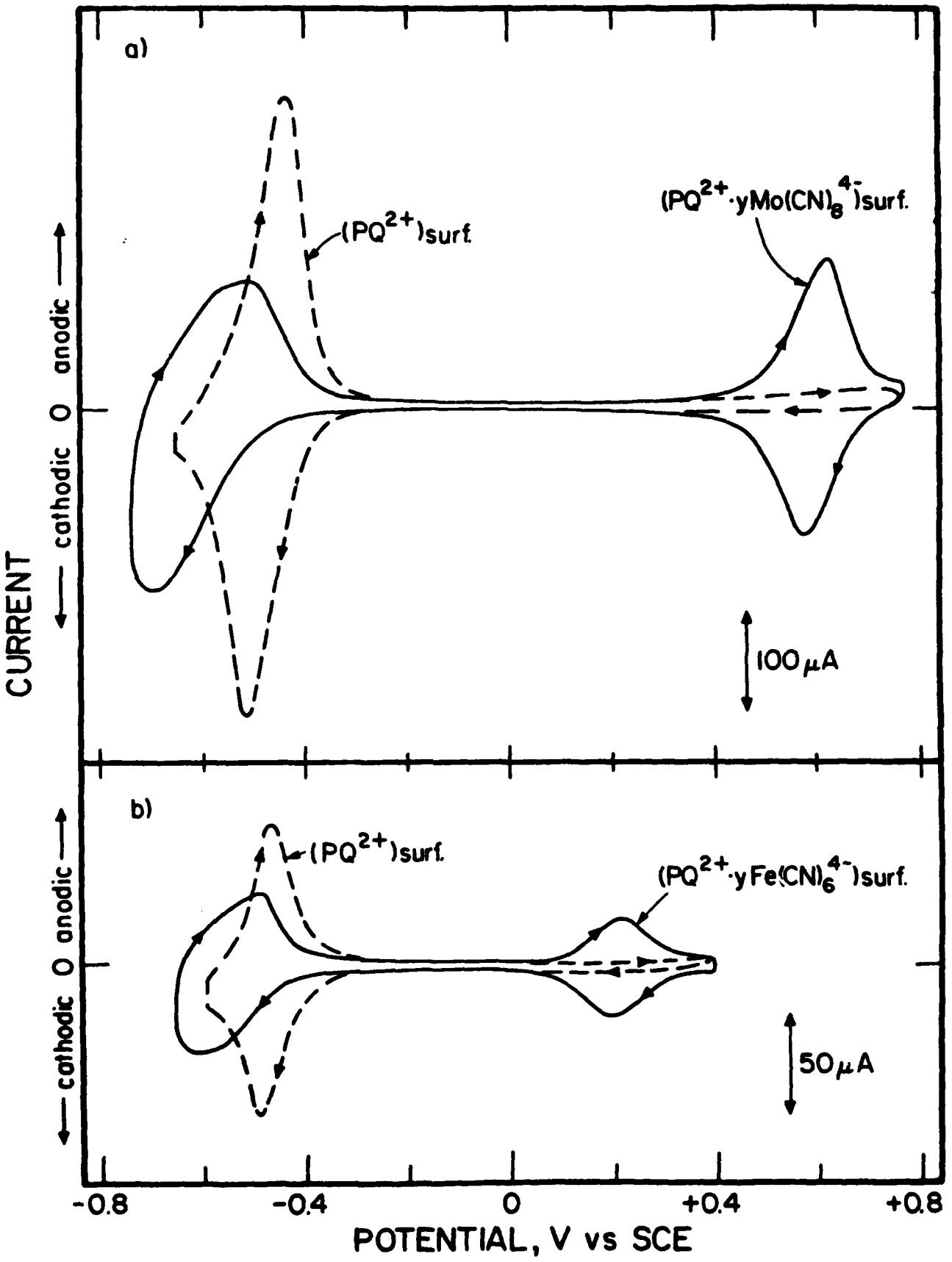
Figure 9. Cyclic voltammograms, 100 mV/s, of a Pt/$(PQ^{2+})_n$ electrode in (a) —— 0.1 M KCl; ---- 0.1 M KCl/50 μM $K_4Fe(CN)_6$; (b) —— 0.1 M KCl/50 μM $K_4Fe(CN)_6$/25 μM $K_3Co(CN)_6$; ---- 0.1 M KCl/50 μM $K_4Fe(CN)_6$; (c) —— 0.1 M KCl/50 μM $K_4Fe(CN)_6$/50 μM $K_3Co(CN)_6$. In (b) and (c) the cyclic voltammograms are the same when starting with either Pt/$(PQ^{2+}\cdot 2Cl^-)_n$ or Pt/$(PQ^{2+}\cdot \tfrac{1}{2}Fe(CN)_6^{4-})_n$. The coverage of $PQ^{2+}$ is $2.8 \times 10^{-8}$ mol/cm$^2$. As for Figure 8, the unpotentiostatted electrode was equilibrated for ~15 min prior to running the cyclic voltammogram.

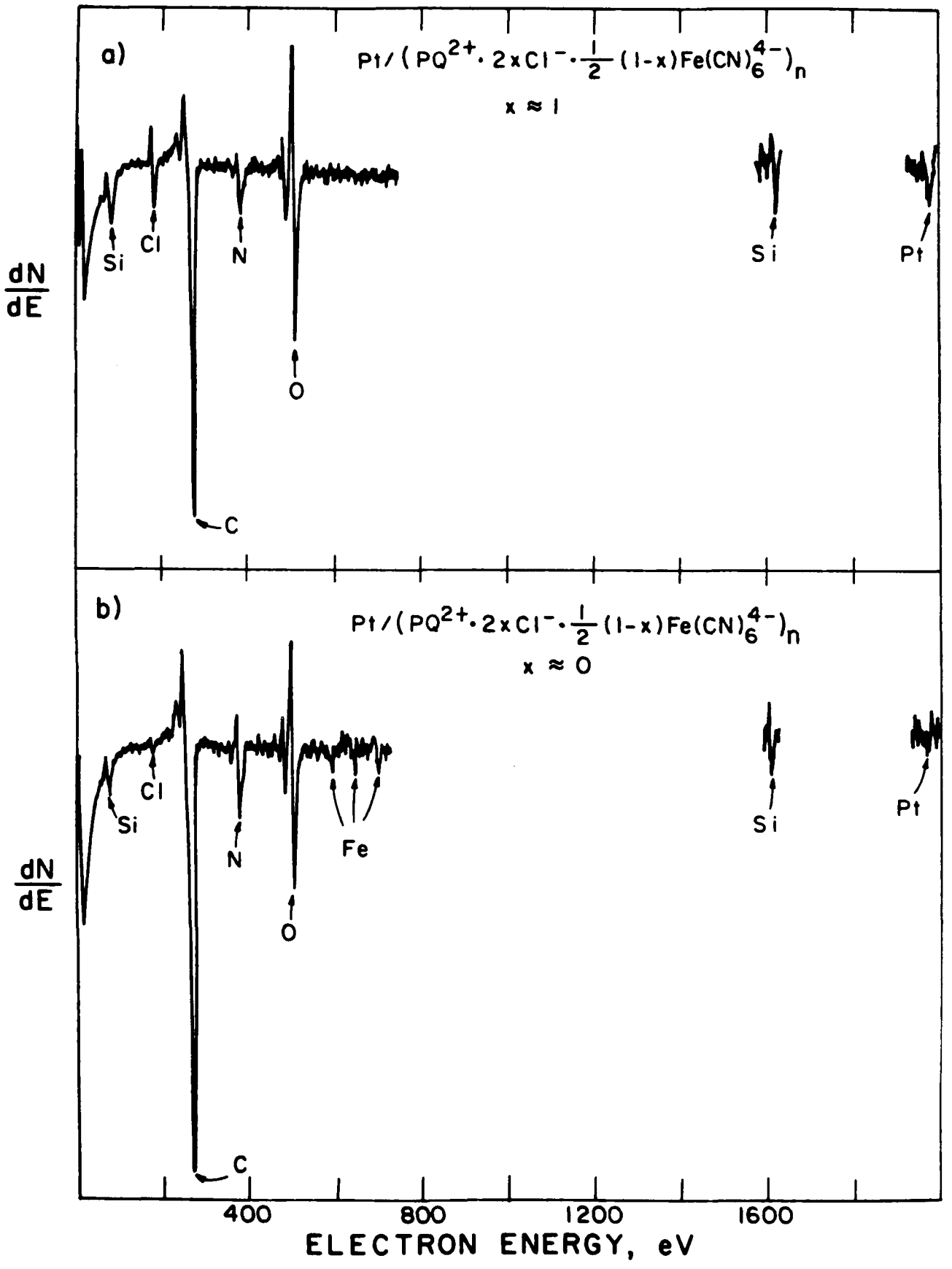

a) 50μM $K_2IrCl_6$
b) 25μM $K_2IrCl_6$
c) 5.0μM $K_2IrCl_6$
d) 2.5μM $K_2IrCl_6$
e) 1.0μM $K_2IrCl_6$
cathodic 0 anodic
200μA/cm²
CURRENT
-0.4
0
+0.4
+0.8
POTENTIAL, V vs SCE

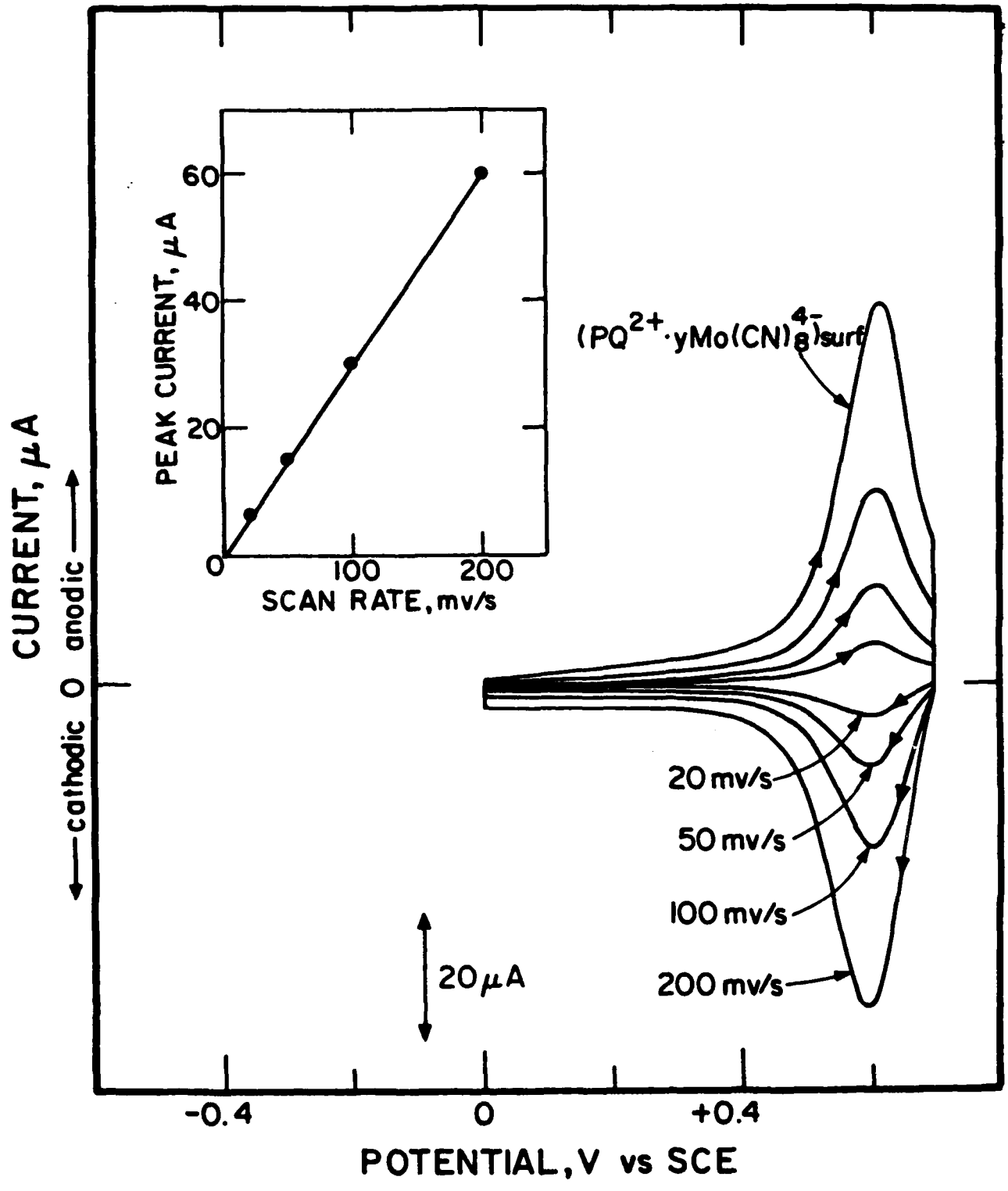

a)
$Pt/(PQ^{2+}\cdot\frac{2}{3}\,x\,IrCl_6^{3-}\cdot(1-x)SO_4^{2-})_n$
x ≈ 0
dN/dE
Si
S
Cl
N
O
C
b)
$Pt/(PQ^{2+}\cdot\frac{2}{3}\,x\,IrCl_6^{3-}\cdot(1-x)SO_4^{2-})_n$
x ≈ 1
dN/dE
Si
Cl
N
O
C
200
400
600
ELECTRON ENERGY, eV

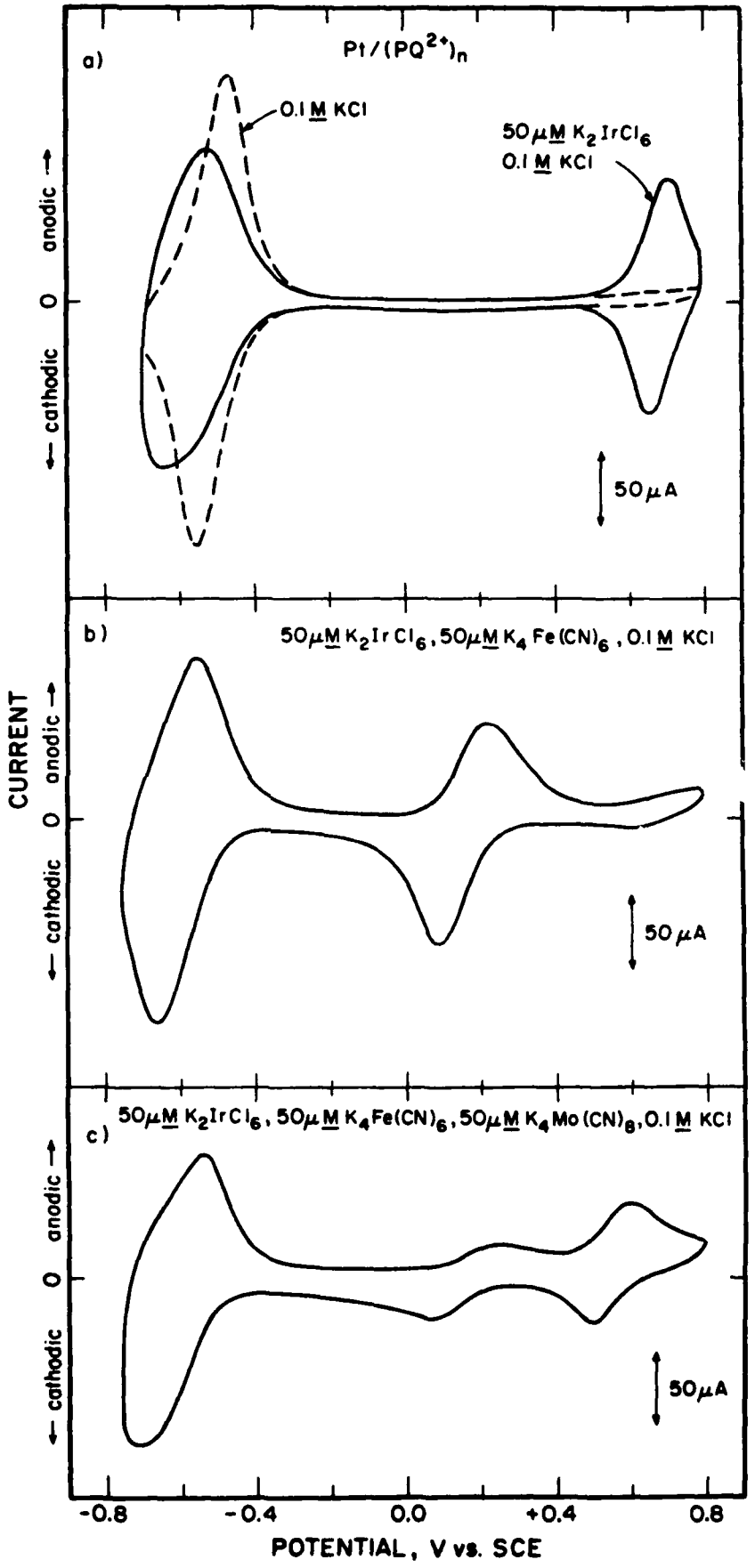

$IrCl_6^{2-/3-}$ wave area / $PQ^{2+/+}$ wave area
0.2
0.4
0.6
0.8
0
10
20
30
40
50
CONCENTRATION OF $K_2IrCl_6$, μM
Cl Auger Signal / C Auger Signal

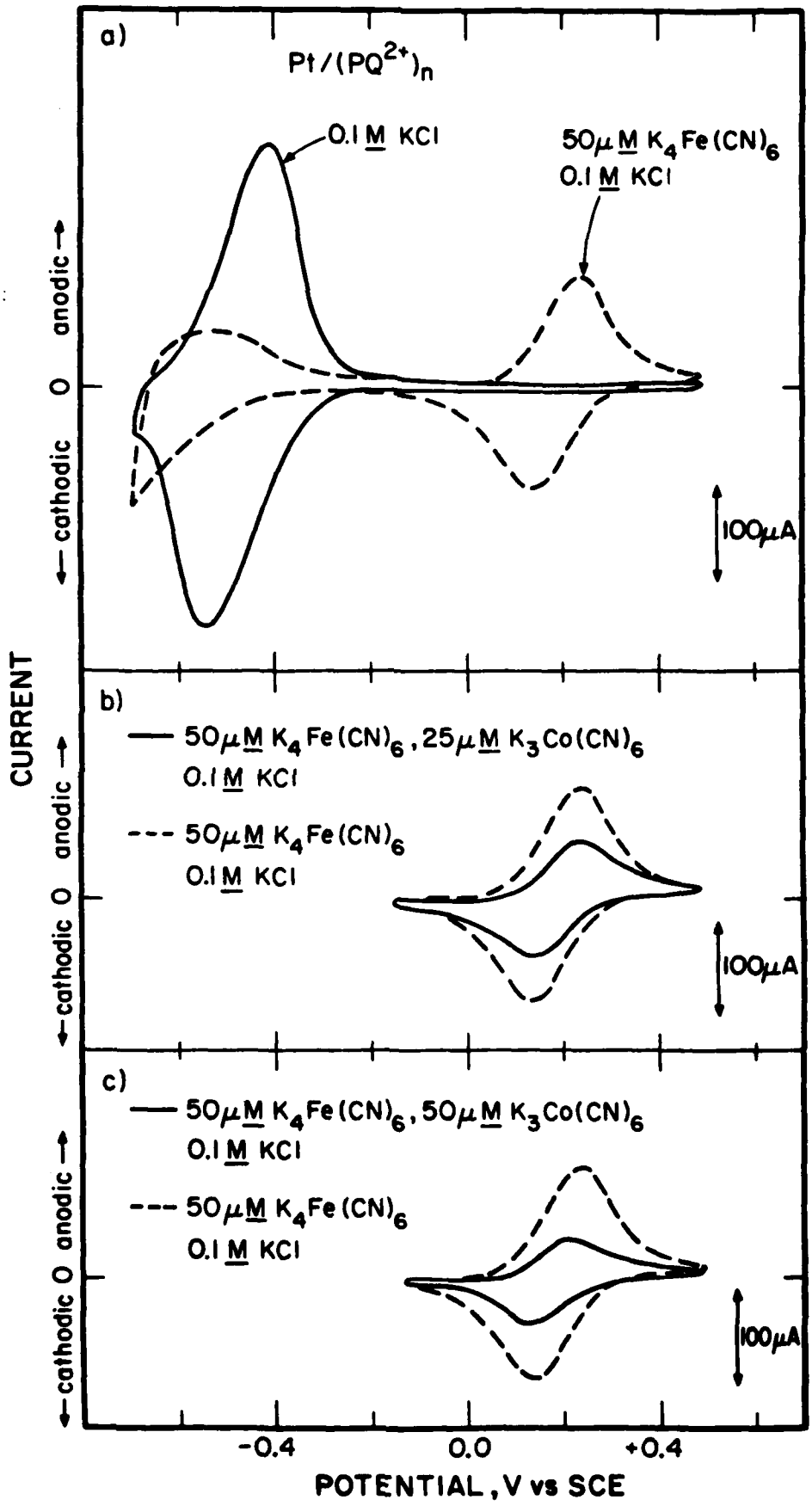

a)
Pt/(PQ2+ · IrCl62−)n
Pt(X2)
Cl(X1)
C (X1)
N (X2)
O (X1)
Si(X2)
b)
Pt/(PQ2+ · SO42−)n
Pt(X2)
S (X2)
C (X1)
N (X2)
O (X1)
Si(X1)
Auger Peak-to-Peak Amplitude, Arbitrary Units
2
4
6
8
10
12
14
Sputtering Time, Minutes


a)
$(PQ^{2+})_{surf.}$
$(PQ^{2+}\cdot yMo(CN)_8^{4-})_{surf.}$
100 μA
b)
$(PQ^{2+})_{surf.}$
$(PQ^{2+}\cdot yFe(CN)_6^{4-})_{surf.}$
50 μA
CURRENT
cathodic 0 anodic
cathodic 0 anodic
-0.8
-0.4
0
+0.4
+0.8
POTENTIAL, V vs SCE


a)
$Pt/(PQ^{2+}\cdot 2xCl^{-}\cdot\frac{1}{2}(1-x)Fe(CN)_6^{4-})_n$
x ≈ 1
Si
Cl
N
O
C
Si
Pt
dN/dE
b)
$Pt/(PQ^{2+}\cdot 2xCl^{-}\cdot\frac{1}{2}(1-x)Fe(CN)_6^{4-})_n$
x ≈ 0
Si
Cl
N
Fe
O
C
Si
Pt
dN/dE
400
800
1200
1600
ELECTRON ENERGY, eV


PEAK CURRENT, μA
60
40
20
0
100
200
SCAN RATE, mv/s
$(PQ^{2+} \cdot yMo(CN)_8^{4-})_{surf}$
20 mv/s
50 mv/s
100 mv/s
200 mv/s
20 μA
CURRENT, μA
cathodic 0 anodic
-0.4
0
+0.4
POTENTIAL, V vs SCE


a)
Pt/(PQ2+)n
0.1 M KCl
50 μM K2IrCl6
0.1 M KCl
anodic
0
cathodic
50 μA
b)
50 μM K2IrCl6, 50 μM K4Fe(CN)6, 0.1 M KCl
CURRENT
anodic
0
cathodic
50 μA
c)
50 μM K2IrCl6, 50 μM K4Fe(CN)6, 50 μM K4Mo(CN)8, 0.1 M KCl
anodic
0
cathodic
50 μA
-0.8
-0.4
0.0
+0.4
0.8
POTENTIAL, V vs. SCE


a)
Pt/(PQ2+)n
0.1 M KCl
50μM K4Fe(CN)6
0.1 M KCl
anodic
cathodic
0
100μA
b)
50μM K4Fe(CN)6, 25μM K3Co(CN)6
0.1 M KCl
50μM K4Fe(CN)6
0.1 M KCl
anodic
cathodic
0
100μA
c)
50μM K4Fe(CN)6, 50μM K3Co(CN)6
0.1 M KCl
50μM K4Fe(CN)6
0.1 M KCl
anodic
cathodic
0
100μA
CURRENT
-0.4
0.0
+0.4
POTENTIAL, V vs SCE

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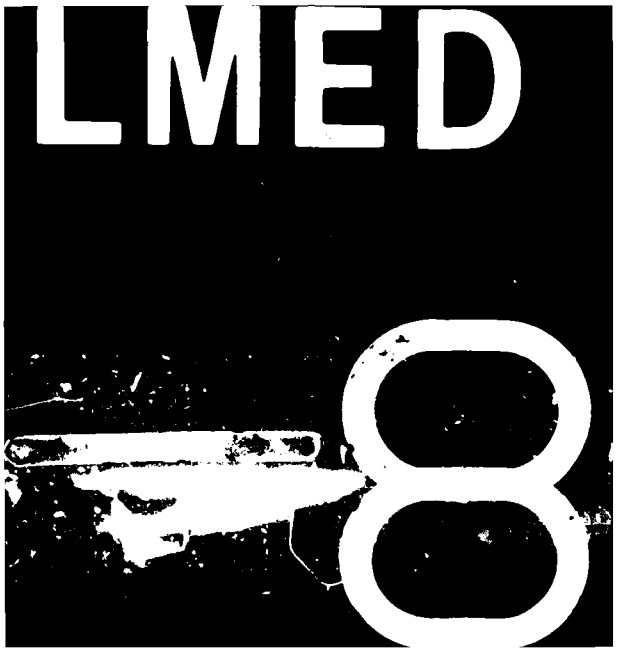
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